Addition of inorganic additives to polymer raw materials, prior to polymer formation, comprises addition of inorganic solidly particles distributed in a matrix of in organic substance.

Publication number: DE10050961

Publication date: 2002-04-25

Inventor: MEYERS FRANZ (US); MICHAEL WEDLER (DE); JÜRGEN KASTNER (DE); WISE MAN PETER (DE)

Applicant: SACHTLEBEN CHEMIE GMBH (DE)

Classification:

- internationally: ***C08F2 / 44; C08K3 / 22; C08K3 / 30;*** **C08F2 / 44; C08K3 / 00;** (IPC1-7): C08J3 / 20; C08J5 / 18; C08K3 / 22; C08K3 / 30; C08K9 / 10; D01F1 / 10; D01F6 / 60

- european: C08K3 / 22; C08K3 / 30

Application number: DE20001050961 20001013

Priority number (s): DE20001050961 20001013

Abstract of **DE10050961**

A process for the addition of inorganic additives to polymer raw materials, prior to polymer formation, comprises addition of inorganic solidly particles having a maximum particle size of 1 mu m distributed in a matrix of in organic substance, to the raw materials from which the polymer is prepared. A process for the addition of inorganic additives to polymer raw materials, prior to polymer formation, comprises addition of a powdered additive comprising inorganic solidly particles having a maximum particle size of 1 mu m distributed in a matrix of in organic substance whereby the organic substance comprises a polyol, polyglycol, polyether, dicarboxylic acid and corresponding derivatives, adipic acid hexamethylenediamine, (AH), salts, caprolactam, paraffins, phosphoric acid esters, hydroxycarboxylic acid esters and cellulose, to the raw material from which the polymer is prepared. In Independently claim is included for the resulting polymer containing inorganic particles.

Description of **DE10050961**

The invention concerns a procedure to the addition by inorganic additives to polymer raw materials before the polymer education.

For the modification of polymers polyester, polyamide 6 and polyamide 6.6 is to be called in particular here, different functional inorganic additives are used. The suitable polymers can be changed by these additives in relation on processing, optical and application-technical qualities. In the synthesis fiber industry are used, e.g., Mattierungsmittel to avoid the speckigen shine undesirable above all for the textilen fibers and the transparence of the polymers. Microcrystals from Titandioxid TiO2 or zinc sulphide ZnS are used moreover. Besides, the application of these microcrystals generates a surface structure on the synthesis fibers which influence the processing qualities with regard to the Friktion of the thread in tasteless guidance elements and the thread run during the Verspinnung and Verstreckung positively. However, for this purpose the microcrystals from posttreated barium sulphate BaSO4 which do not lead towards TiO2 and ZnS, however, to the Mattierung of the polymers can be also used. Another example is the application of Nanokristallen from Titandioxid to produce polymers with UV-protecting qualities.

So that the desired effects attainable with the single additives can become clear, special meaning is to be portioned out to the technology of the addition of the additives to the polymer. Here in

principle there are three addition possibilities:

1. Addition of the additives to the raw materials for the polymer production, i.e. before the real polymer education
2. Addition of the additives during the polymer education process
3. Addition of the additives to the ready polymer glazes, i.e. after ending of the chain growth

According to the state of the technology the addition of the inorganic additives occurs for the modification of polymers almost exclusively after the addition possibilities 2 and 3 (exception: Catalysts for the polymer education). For example, the addition of the TiO2-pigments / microcrystals occurs in the production of synthesis fibers in the process in form of a watery or organic suspension (Slurry) in an early stage before the Polymerisationsreaktion (addition possibility 2). Also BaSO4 additives or Nanokristalle of TiO2 are put down on this way on a polymer.

The addition possibility 2 (addition of an additive suspension during the polymer education process) proved up to now in many cases the best polymer qualities in relation on Weiterverarbeitbarkeit and other qualities of the made polymers. However, the polymer manufacturer must pursue a considerable technical and personnel expenditure to prepare the additive suspension for the application. The steps Dispergierung the additive particle count to it in the suspension medium, separation of the coarse grain factions and avoidance of Reflockulation in the suspension. Besides, is to be paid attention to the fact that it does not come with the addition of the prepared suspension to the mass stream to Flockulationseffekten, by interaction with other additives or by temperature influence (cold suspension <50 C DEG is given in hot mass stream> 200 C DEG) can appear.

The possibility 3 (addition of the additives to the ready polymer glazes, also glazes modification procedure or Schmelzemattierungsverfahren called) is described, e.g., in the DE 40 39 857 C2. Nevertheless, the glazes modification procedure shows the following disadvantages:
The additives (inorganic solid particles) are trained as a powder in the ready polymer glazes. To the setting of the desired solid salary in the polymer, above all, a steady powder dosage is necessary.

Condition for it is good to very good assembly-line ability of the powders. The used powders on the basis of TiO2, BaSO4 and ZnS show all bad assembly-line abilities and can lead in the powder supply system to undesirable bridges and shaft education. It was found (measurements with a Ringschergerät) that these powders are to be classified as very much kohäsiv to not fluently. Therefore, is with the dosage of these powders with considerable Dosierschwankungen to count which would not lead on account of the solid concentration divergences linked with it to substantial amounts of product appropriate for specification.

So that the qualities of the additives can be fully effective in the polymer, a very good and steady distribution of the single particle is necessary in the polymer. The Dispergierung of the powders with the different glazes modification procedures and in the production of Masterbatchen occurs in especially laid out extrusions. The Dispergierbarkeit of the used powders must be so good that the mole forces are sufficient in these extrusions to achieve the necessary particle dimensions distribution in the polymer. The powders used according to the state of the technology on the basis of TiO2, BaSO4 and ZnS are in the form of delivery in agglomerated form, i.e. strong mole forces must be used to smash these Agglomerate and to distribute optimally. Compared with the conventional additive addition about additive suspension during the polymer education process (addition possibility 2) the described glazes modification procedures in relation on particle distribution qualitatively prove worse polymer products because the mole forces are higher to the Dispergierung of the additive suspension by suitable choice of the Dispergiermaschinen than in extrusions or Knetern.

With the subsequent treatment of the made polymers the interest to coarse additive particles leads a role relevant for quality. This particle lead, e.g., in the production of synthesis fibers by Verspinnung and Verstreckung to a raised number in undesirable thread breaks. At the same time the state time is also lowered by polymer filters and Spinpack filters. In the production of additive suspension for the addition during the polymer education process (addition possibility 2) can be removed this coarse particle not exhausted by Dispergierung by Zentrifugation, Sedimentation and/or filtration from the niedrigviskosen suspension. After the Dispergierung in the extrusion (addition possibility 3) cannot be separated the still verbleibenen coarse particle any more, because in these hochviskosen polymer glazes the necessary filter delicacies cannot be reached. That is the powders used according to the state of the technology on the basis of TiO2, BaSO4 and ZnS also have after the Dispergierung in the extrusion an undesirable coarse interest which influences the quality of the polymer end products negatively.

On account of these disadvantages the glazes modification procedure hardly could assert itself in practice up to now.

The addition of additive suspension to the polymer raw materials or to their preparations (addition possibility 1) has compared with the addition possibility 2 considerable disadvantages in relation on Verteilunsgrad of the additives in the later polymer. Many of the called inorganic additives - insbesonders TiO2 - have in the sour area only one low stability against Flockulation. Because in the production of polyester and polyamide the raw materials or initial interproducts still contain a considerable number in free acid groups, it comes with this addition possibility for undesirable Reagglomerationen. That is the good Dispergierung of the particle in the suspension cannot be maintained in the polymers. For this reason the addition of additive suspension has not asserted itself to the polymer raw materials or to their preparations in practice.

The addition of powders on the basis of TiO2 or BaSO4 to the raw materials or their preparations (likewise addition possibility 1) does not lead to the desired polymer qualities and polymer qualities, because the mole forces which work during the next Polymerherstellprozesses are not sufficient to distribute the Agglomerate and Flockulate which seem necessarily in the added powders, in the mass stream to dispergieren and homogeneous in the polymer. Therefore, this procedure variation is not likewise practicable.

Task of the invention is to remove the disadvantages of the state of the technology and to create in particular a procedure for the modification of polymers by fine-piece inorganic solid particles which permits an enough precise dosage of the additives to be added and guarantees this a homogeneous distribution of the additives without undesirable coarse interest in the preserved polymer, without the additives must be prepared by the polymer manufacturer in special way.

The task is solved by a procedure to the addition of inorganic additives to polymer raw materials before the polymer education
with him an additive in powder form,
which fine-distributes the inorganic solid particles by a maximum grain size of 1 mu m in a matrix from an organic matter embedded contains and the organic matter contains one or several the materials Polyole, polyglycols, Polyether, Dicarbonsäuren and their derivatives, ah-salt (nylon salt, from adipic acid and Hexamethylendiamin), Caprolactam, paraffins, Phosphorsäureester, Hydroxycarbonsäureester and Cellulose,
to the raw materials of which the polymer is produced is added (addition possibility 1).

The production of the additives in powder form (Präparationsmittel, Mattierungsadditive) is described in that WHERE 00/14165 or also in that WHERE 00/14153. The Präparationsmittel (Mattierungsadditive, additives in powder form) for the subsequent treatment in synthetic polymers, consisting of fine-piece inorganic solid states, well-chosen from pigments and/or fillers, are embedded in a carrier material, well-chosen from at least one of the organic matters Polyole, polyglycols, Polyether, Dicarbonsäuren and their derivatives, ah-salt, Caprolactam, paraffins,

Phosphorsäureester, Hydroxycarbonsäureester and Cellulose fine-distributed. Fine-distributed is called that the solid particles are in not agglomerated form in an organic matrix. The production of these additives in powder form become in a watery premixture which contains the organic matter in such an amount that the interest of the organic matter from 0.2 to 50 Gew.-% (covered to the inorganic solid state content of the ready additive in powder form) amounts, from 20 to 60 Gew.-% (covered to the whole beginning of the watery premixture) of the inorganic solid states dispergiert, then the dispersion on a middle grain size d50 from 0.2 to 0.5 mu m becomes wet-ground, the Überkornanteil from> 1 mu m from the suspension has dried and the suspension. The preserved additives in powder form have a middle particle size from up to 100 mu m.

It was thought that these additives in powder form can be well measured on account of her very good assembly-line ability (in contrast to fine-ground powders available up to now) accordingly.

Because the inorganic solid particles are fine-distributed in the particle size suitable for the later application (e.g., 0.3 mu m TiO2 microcrystals for the Mattierung of synthesis fibers) in the additives in powder form in the organic matrix and are embedded in non-agglomerated form, they must be released only by melting / dissolve the organic matrix at the risk of weak mole forces in the mass stream and be distributed homogeneous. The suitable powders can be used by the polymer manufacturer without special preparation during the polymer production, without it comes to high-class losses compared with a procedure according to the state of the technology (addition possibility 2). Practically this means that their achievement optimum (Mattierungsgrad, UV protection etc.) already with one in comparison to state of the technology lower application amount is reached by the finer distribution of the additives.

Specifically the addition of the additives in powder form can be carried out as follows:
For polyester (Polyethylenterephthalat (PET), Polybutylenterephthalat (PBT), Polytrimethylenterephthalat (PTT)):

- Addition as a powder to the paste, consisting of Terephthalsäure (PTA), Diolkomponente (Ethylenglykol, 1.4-Butandiol or 1.3-Propandiol) and already to veresterten interproducts (PTA procedure).
- Addition as a powder in the Aufschmelzbehälter, in the Dimethylterephthalat (DMT) for the DMT procedure aufgeschmolzen becomes.

For polyamide (PA):

- Addition as a powder for the ah salt solution (adipinsaures Hexamethylendiamin or Hexamethylenammoniumadipat) to the production of PA 6.6.
- Addition as a powder in the Aufschmelzbehälter, in the Caprolactam for the production of PA 6, aufgeschmolzen becomes.

The solid particles important for the aimed polymer qualities are released by the special arrangement erfindungsgemäss to used additives (imbedding in a polymer-acceptable organic matrix) bit by bit, so that the Flockulationsneigung can be minimised in the system. Because the addition of the powders can occur without temperature difference to the raw material system, the Flockulationsneigung is suppressed, in addition.

Prefers the inorganic solid particles contain TiO2, and/or BaSO4 and the solid particles can be also posttreated.

Preferentially the organic matter contains Antioxidantien (e.g., Butylhydroxyanisol or Hydroxyanisol) in an amount from up to 0.5 Gew.-% (referring on the amount of organic matter).

The organic matter can contain other usual auxiliary materials and additives. Preferentially the organic matter at least 98 Gew.-% Polyethylenglycol or ah-salt or Caprolactam contains, especially preferentially the organic matter exists of Polyethylenglycol or ah-salt or Caprolactam and up to 0.5 Gew.-% of an Antioxidans.

As a polymer polyester or polyamide 6 or polyamide 6.6 is used preferentially.

Followers to additive compositions in powder form are used for the erfindungsgemässe procedure preferentially:

EMI8.1

Especially additives in powder form with from 75 to 85 Gew-% of inorganic solid and from 15 to 25 Gew.-% of organic matter are preferred. A preferential middle grain size d50 of the inorganic solid which is embedded in the organic matter amounts to from 0.25 to 0.45 mu m.

Polyfirst fibers and polyester films, or polyamide fibers and polyamide films which likewise contain the inorganic solid particles can be produced of an inorganic solid particle containing polyester, or polyamide which, or which under erfindungsgemässer use of the additives in powder form was produced.

Claims of **DE10050961**

1. Procedures to the addition of inorganic additives to polymer raw materials before the polymer education, thereby marked, that
an additive in powder form,
which fine-distributes the inorganic solid particles by a maximum grain size of 1 mu m in a matrix from an organic matter embedded includes,
and the organic matter passes, of one or several the materials Polyole, polyglycols, Polyether, Dicarbonsäuren and their derivatives, ah-salt, Caprolactam, paraffins, Phosphorsäureester, Hydroxycarbonsäureester and Cellulose,
to the raw materials of which the polymer is produced is added.

2. Procedures after claim 1, thereby marked that the inorganic solid particles TiO2 contain, and/or BaSO4 and the solid particles can be also posttreated.

3. Procedures after claim 1 or 2, thereby marked that the organic matter exists of Polyethylenglycol or ah-salt or Caprolactam and up to 0.5 Gew.-% of an Antioxidans.

4. Procedures after one of the claims from 1 to 3, thereby marked that as a polymer polyester or polyamide 6 or polyamide 6.6 is produced.

5. Polymer, containing inorganic solid particles, thereby marked that the polymer is produced after a procedure, according to one or several the claims from 1 to 4.

6. Polyester, containing inorganic solid particles, thereby marked that the polyester is produced after a procedure, according to one or several the claims from 1 to 4.

7. Polyester fiber or polyester film, containing inorganic solid particles, thereby marked that the

polyester fiber or the polyester film is produced of a polyester according to claim 6.

8. Polyamide, containing inorganic solid particles, thereby marked that the polyamide is produced after a procedure, according to one or several the claims from 1 to 4.

9. Polyamide fiber or polyester film, containing inorganic solid particles, thereby marked that the polyamide fiber or the polyester film is produced of a polyamide according to claim 8.